Ionic radii of heavy actinide(III) cations

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Filling of the $4f$ orbitals in the lanthanide series and $5f$ orbitals in the actinide series is accompanied by a significant decrease in the atomic and ionic radii. This effect, called lanthanide (actinide) contraction, is the consequence of incomplete shielding of the outermost p orbitals from nuclear charge by the $4f$ and $5f$ electrons, respectively. In addition to the increase of the effective nuclear charge, relativistic effects contribute considerably to the actinide contraction[1,2]. Relativistic effects influence the contraction of the lanthanide(III) and actinide(III) ionic radii in two ways: by splitting the outermost p orbitals and stabilisation of $p_{1/2}$ orbitals, and by expanding the $f_{5/2}$ and $f_{7/2}$ orbitals. The latter results in less effective shielding from the nuclear charge. For the heaviest actinides this may lead to much smaller ionic radii than in the absence of relativistic effects. For example, in the case of Fm^{3+} the relativistic calculations give r_i 8 pm smaller than nonrelativistic, whereas in the case of Er^{3+} (homologue in the lanthanides series) - only 2.5 pm.

For the five heaviest members of the lanthanide series, the spacing between ionic radii of the adjacent elements decreases regularly from 1.3 to 1.0 pm (Table 1). Unexpectedly, in the case of end actinides the spacings between r_i of the neighbouring elements change irregularly. For example, the difference in r_i between Es^{3+} and Fm^{3+} is 1.7 pm, whereas that between Md^{3+} and No^{3+} only 0.2 pm.

Table 1. Ionic radii of heavy lanthanides and actinides, CN=6

Ln^{3+} ion	r_i , pm [3]	An^{3+} ion	r_i pm
Ho^{3+}	89.4	Es^{3+}	92.8
Er^{3+}	88.1	Fm^{3+}	91.1
Tm^{3+}	86.9	Md^{3+}	89.6
Yb^{3+}	85.8	No^{3+}	89.4
Lu^{3+}	84.8	Lr^{3+}	88.1

Ionic radii are usually obtained from X-ray diffraction data for oxides or fluorides [4]. In the case of heavy actinides from Bk^{3+} to Es^{3+} r_i were determined from lattice parameters of sesquioxides measured by electron diffraction [5]. Unfortunately, elements heavier than einsteinium are produced in non-weighable amounts, so that the experimental structural data for these elements are not available. For Fm^{3+}, Md^{3+}, No^{3+} and Lr^{3+}, the values of r_i were determined only by the chromatographic method [6,7,8]. The ionic radii of Fm^{3+}, Md^{3+} and Lr^{3+} were estimated by comparing their elution positions with the positions of rare earth tracers and of actinides of known ionic radii on strong acidic cation exchange resin with α-hydroxyisobutyrate solution as eluent [6,8]. In the case of No, which is unstable in the +3 oxidation state, r_i was also determined chromatographically but on the cryptomelane MnO_2 - inorganic ion exchanger which shows strong oxidizing properties. The HNO_3-H_5IO_6 solution was used both as oxidant and eluent [7].

In order to understand the sources of irregularity in the contraction of ionic radii of heavy actinides we compared the experimental r_i with the radii of the maximum charge density, R_{max}, of the outermost orbital radii in these cations. Linear correlations of r_i on R_{max} and on expectation values of orbital radii, <r>, were found for cations of the same charge in many groups of the periodic table [9,10]. These

correlations are suitable to predict r_i of ions in case when experimental measurements are difficult or impossible [9,11,12].
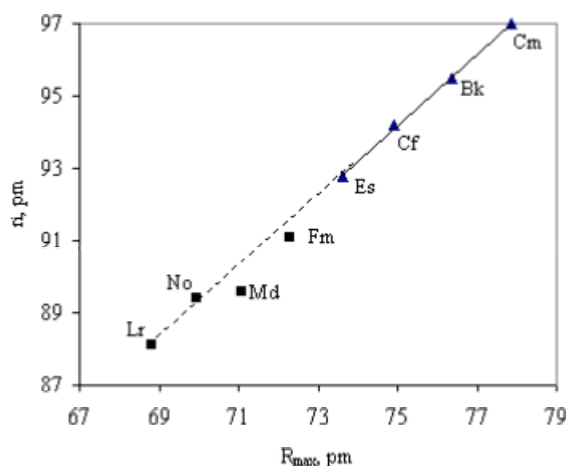

Figure 1. The ionic radius as a function of the 2j+1 weighted in the heavy actinides. Triangles present ionic radii determined from electron diffraction data, squares ionic radii from elution experiments.

Figure 1 presents the dependence of the ionic radius on R_{max} of the outermost shell in the ions of the heavy actinides. The orbital radii have been calculated by V.Pershina using the Dirac-Slater method [13]. As the outermost shell radii we used the 2j+1 weighted R_{max}. The ionic radii of Cm^{3+} Bk^{3+}, Cf^{3+} and Es^3 are those of Templeton and Dauben radii [3], whereas the ionic radii of the last four actinides where obtained from elution experiments by comparing with Templeton and Dauben radii of lanthanides. As shown in Figure 1 a linear dependence of r_i on R_{max} of the outermost shell is observed for +3 actinides from Cm to Es. For these cations the experimental r_i were determined from electron diffraction on oxides. It is important to note that the chromatographically determined ionic radii of Lr^{3+} and No^{3+} also fit the extrapolated part of the straight-line plot. As shown in Table 2. large differences between the extrapolated and experimental radii are observed for Md^{3+} and Fm^{3+}.

Table 2. Experimental and extrapolated r_i for heaviest actinides, CN=6

An^{3+} ion	R_i(pm) experimental	r_i(pm) extrapolated
Fm^{3+}	91.1	91.5
Md^{3+}	89.6	90.3
No^{3+}	89.4	89.2
Lr^{3+}	88.1	88.1

As mentioned earlier the ionic radii of Fm^{3+}, Md^{3+} and Lr^{3+} were determined only by the chromatographic method. The linear dependence of the logarithm of distribution coefficients ,K_d, on r_i for the tripositive ions of heavy lanthanides and actinides in α-hydroxyisobutyrate solutions was the basis for the r_i determination of the heaviest actinides [6,8]. However, in complexing solutions strong deviations from linearity of the log K_d vs. r_i plot are observed [4,15]. This effect called double-double or tetrad consist in the division the lanthanide and actinide series into two subgroups by the f^7 configuration and futher division of each subgroup into two segments by the f^3-f^4 and f^{10}-f^{11} pairs [16]. Stabilization of the f^3, f^4, f^7 ,f^{10} and f^{11} configurations depends on the environment and decreases with increasing ability of the ligand to expand the f electrons cloud. In water, where the nepheloauxetic effect is very low the

delocalization of f electrons is insignificant. In α-hydroxyisobutyrate solution where water molecules in the solvation sphere are exchanged for the ligand which shows high nepheloauxetic effect, the cations with f^3, f^4, f^7, f^{10} and f^{11} configurations form less stable complexes than expected from ionic radii.
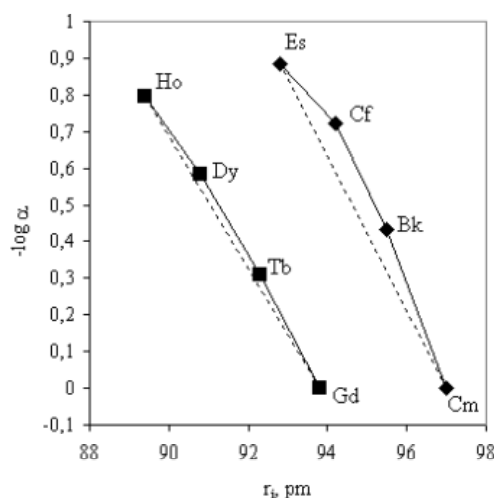

Figure 2. Dependence of the logarithm of the separation factor (α) on r_i for the third segment (f^7-f^{10}) in lanthanide (Gd^{3+}-Ho^{3+}) and actinide (Cm^{3+}-Es^{3+}) series in the α-hydroxyisobutyrate ~V strong acidic cation exchange resin system.

Figure 2 presents the dependence of the logarithm of the separation factor (α) on r_i for the third segment (f^7-f^{10}) in both lanthanide (Gd^{3+}-Ho^{3+}) and actinide (Cm^{3+}-Es^{3+}) series in the α-hydroxyisobutyrate ~V strong acidic cation exchange resin system. The separation factor α is defined as $K_d(Ln^{3+})/K_d(Gd^{3+})$ or as $K_d(An^{3+})/K_d(Cm^{3+})$ for lanthanides and actinides, respectively. Figure 2 shows that for the third segment the dependence of log α on r_i for lanthanides(III) does not deviate much from linear. However, in the case of actinides(III) strong deviations from linearity due to the tetrad effect are observed. This is because greater radial extent expansion of $5f$ in comparison with $4f$ orbitals results in stronger participation of $5f$ orbitals in metal to ligand bonding. Similar effect should be observed in the fourth segment (f^{11}-f^{14}) of the lanthanide (Er^{3+}-Lu^{3+}) and actinide (Fm^{3+}-Lr^{3+}) series. In the case of lanthanides(III) small deviations from linearity are indeed observed [17], whereas for Fm^{3+}- Lr^{3+} strong tetrad effect is to be expected. This means that ionic radii of the heaviest actinides can not be determined from linear dependence of log K_d or log α on r_i in experiments based on the α-hydroxyisobutyrate ~Vcation exchange system, as there is no way to get rid of the tetrad effect in the stability constants. The only way seems to be extrapolation of the linear dependence of r_i (ionic radius based on crystal data) on R_{max}, which is valid for the Cm-Es interval, to the Fm-Lr interval, see Figure 1. From this extrapolation one gets r_i equal to 91.5 and 90.3 pm for Fm^{3+} and Md^{3+}, respectively.

The question remains, why the ionic radii of Lr^{3+} and No^{3+}, determined from elution positions, are the same (Lr^{3+}) or almost the same (No^{3+}) as those calculated from orbital radii. In the case of Lr^{3+} participation of the f orbitals in the metal to ligand bonding is negligible because the $5f$ shell is filled and the nepheloauxetic effect in $5f$ electrons does not affect stability constant of the α-hydroxyisobutyrate complex. As far as the No^{3+} is concerned it should be noted that it has been determined chromatographically by comparison of its K_d with K_d of heavy lanthanides on cryptomelane-MnO_2 cation exchanger [7]. The selectivity of cryptomelane-MnO_2 for the cations is due to steric effects and depends on the radii of the cations and of the tunnel (280 pm) in the sorbent [18]. The hydrated +3 metal cations with diameters much larger than 280 pm must be dehydrated before entering the ion exchange phase.

Therefore, the selectivity of the cyptomelane MnO_2 depends nearly linearly on the free energy of hydration which, in turn, is a linear function of the reciprocal of the ionic radius. The linear dependence of the free energy of hydration on the reciprocal of the ionic radius for the whole Ln^{3+} series and for those actinides for which the ΔG_{hydr} is available, indicates that in the hydration energy the tetrad effect is, as expected, insignificant.

Conclusion

The tetrad effect in complexation of actinide(III) cations by α-hydroxyisobutyrate gives underestimated values for Fm^{3+} and Md^{3+} ionic radii comparing with the ionic radii obtained from the linear dependence of ionic radii on orbital radii. With the calculated r_i for Fm^{3+} 91.5 pm and Md^{3+} 90.3 pm, the ionic radii of An^{3+} at the end of the series decrease regularly like in the radii of the lanthanide (III) cations (Fig.3).
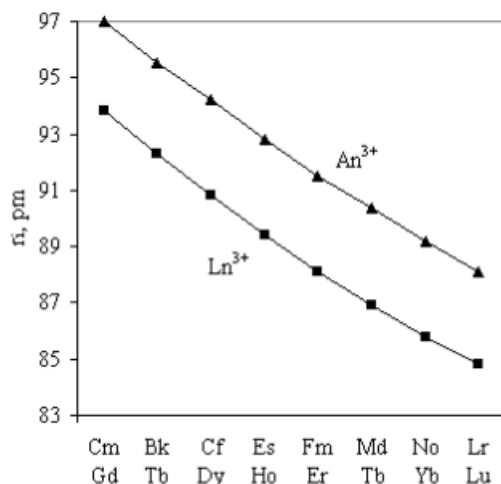

Figure 3. Contraction of ionic radii of the heavy lanthanides(III) and actinides(III). The radii of Fm^{3+} and Md^{3+} are calculated from R_{max} by extrapolation procedure.

Acknowledgments

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